



中空粒子構造を利用したナノ粒子空間分布の可逆的制御

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論 文 内 容 要 旨

Background and objectives of the present work are described in Chapter 1. Particles smaller than 100 nm, which are called “nanoparticles,” exhibit physical and chemical properties different from bulk materials. To expand the potential of the nanomaterials, it is required to programmably create assemblies of NPs in a limited space. The specific properties of NPs can be effectively utilized in locally condensed areas in the particle assembly. Some researchers indicated that the condensed states of NPs exhibit interesting phenomena different from the dispersed states of NPs, for instance, light trapping in solar cells and photocatalysts, and optical magnetism in metamaterials. Plasmonic nanoparticles (NPs) such as silver and gold are well known as materials having unique properties (e.g. catalytic, magnetic, optical, and sensing properties). Oscillation of the NP free electrons induced by light irradiation generates a local electric field on the NP surface, resulting in unique properties of the NPs. Irradiation light with a specific wavelength is absorbed by the NPs, which is a typical phenomenon of plasmonic NPs called Localized Surface Plasmon Resonance (LSPR). Surface-enhanced Raman scattering (SERS) has received enormous interest since it was discovered in the 1970s because strong Raman intensities are obtained from molecules neighboring the NP surfaces. In the case of plasmonic NPs, creation of hotspots at which the electric field is enhanced by assembling the NPs can be a practical way to improve the plasmonic properties.

Approaches to control over the spatial distribution of micron- or submicron-sized particles have been reported by many researchers. However, rapid aggregation in the process of assembling generally accompanies irreversible agglomeration of the NPs, causing a deterioration of intrinsic properties depending on particle sizes. Nano-sized particles, in particular, tend to be more easily aggregated than submicron- or larger-sized particles because of the low colloidal stability of NPs. Based on the background, the goal of the present work is development of a new system for reversible control over the spatial distribution of gold (Au) NPs in a liquid phase. In this thesis, the spatial distribution of the NPs is defined as the assembled or dispersed states of the NPs. We have focused on the hollow silica (SiO₂) particle incorporating Au NPs for the system. Because SiO₂ particles

are widely known as materials with high colloidal stability, SiO₂ can prevent the Au NPs from agglomeration. In addition, all the surface of the Au NP in the hollow SiO₂ particle is exposed to the liquid phase, therefore the specific properties of the NPs can be efficiently used.

In Chapter 2, previous reports on controlling the assemblies of plasmonic NPs are categorized into static and dynamic controls. The static controls are further categorized as top-down and bottom-up approaches. As for the top-down approaches, lithography techniques such as electron beam lithography, ion beam lithography, and nanosphere lithography are focused on. By contrast, chemical bonds between the NPs and capillary-force driven assembling methods are some of the examples of bottom-up approaches. Employing the statically controlled techniques can achieve precise design of plasmonic assemblies, whereas some expensive experimental equipment is necessary. Compared with the static control methods, the external stimulation of NPs is cost-effective and offers a variety of operational factors to control the assembled states of the NPs. In this chapter, the control of plasmonic NP assemblies via external stimuli such as pH, temperature, light, magnetic field, and electric field are summarized. Among them, an external AC electric field has a potential of diversifying the assembled states of NPs due to a variety of operational factors such as field strength, application frequency, and application time.

Based on the previous reports summarized in Chapter 2, the dynamic control with application of an external AC electric field is employed for reversible control over the spatial distribution of Au NPs. In Chapter 3, the assembling phenomenon of Au NPs in a liquid under application of an AC electric field is investigated. The optical and sensing properties of Au NPs in suspension were measured after the field application with different field conditions. The UV-Vis spectra were altered by the field application, suggesting that the Au NPs formed clusters. In particular, the spectra of Au NPs were broadened by 0.1 kHz field application. The optical properties and the sizes of Au NP assemblies were strongly correlated to each other according to a combined result of the UV-Vis spectra and size distributions measured with a dynamic light scattering (DLS) photometer. Lower Raman intensities were observed for the Au NP suspension treated by field application of a low-frequency of 0.1 kHz in 30 V/mm compared to those without the electric field. The result was probably due to rapid aggregation and sedimentation of Au NPs. Conversely, the field application at high frequencies of 1 kHz or 1 MHz successfully enhanced the Raman intensities by approximately 150%. The assembled states of Au NPs were gradually changed by the high-frequency field application time, suggesting that field application for an appropriate period can be a practical way to control the clustered states of plasmonic NPs. The present results showed that application of an external AC electric field is a promising approach to obtain specific properties from plasmonic NPs in a liquid phase. However, it was not likely that the Au NP clusters formed via the electric field were redispersed in their suspension due to the strong aggregation of Au NPs.

For the reversible control over the spatial distribution of Au NPs, hollow SiO₂ particles incorporating a Au NP are synthesized in Chapter 4. To clarify the relation between the assembled states of the NPs and their sensing property, Au NPs

were functionalized with a probe molecule, 4-Mercaptobenzoic Acid (PMBA), before silica coating. The hollow particles incorporating a Au-PMBA NP (Au-PMBA@hSiO₂) are prepared by a selective etching process using polyethylenimine (PEI). The Au-PMBA@hSiO₂ particles were synthesized by the following steps: (1) synthesis of SiO₂ particles incorporating a Au NP (Au-PMBA@SiO₂), (2) modification of the Au-PMBA@SiO₂ with PEI, and (3) etching of the PEI-modified Au-PMBA@SiO₂ with water. The PEI molecules on SiO₂ surface in water creates a locally basic condition, and protect the surfaces of Au@SiO₂. Only the inner part of Au@SiO₂ particles modified with PEI was gradually etched with water during immersion of Au@SiO₂ in water for 15 h. Spherical hollow particles, however, was deformed by etching them for 18 h or longer. The hollow particles incorporating multiple Au NPs (mAu-PMBA@hSiO₂) are also synthesized. In order to incorporate of multiple Au NPs in a SiO₂ shell, we adjusted the concentration of Au NPs added in the synthetic step for Au-PMBA@SiO₂. The number of Au NPs in the SiO₂ shell was controlled by adjusting the Au NP concentration. The plasmonic properties of the hollow SiO₂ particles depended on the number of Au NPs inside the shell. The extinction peaks of Au-PMBA@hSiO₂ were sharply observed at approximately 530 nm, whereas broad peaks were observed for mAu-PMBA@hSiO₂. Raman intensities of PMBA were dramatically enhanced by incorporating multiple Au NPs into the hollow particle (mAu-PMBA@hSiO₂). This suggested that hotspots were created between Au NPs in the SiO₂ shell compartment.

In Chapter 5, the inner Au NPs in the hollow SiO₂ sphere are focused on. First, the movements of inner Au NPs in the hollow sphere are observed with a liquid cell transmission electron microscopy (LCTEM). The LCTEM observation experimentally showed the movement of a single Au NP in the shell compartment, which suggested that the hollow particle-structure is usable for exposing a whole surface of a Au NP. Multiple Au NPs connected each other in the hollow SiO₂ moved as a Au NP cluster instead of dispersed NPs. Next, the strengths of electric fields induced by incident light are calculated using Maxwell's equation with a finite element method. A maximum strength of the electric field induced in the vicinity of a single Au NP was calculated to 7 V/m, whereas that of Au NP dimer was 700 V/m. The strength of electric fields between Au NPs was increased by increasing the number of Au NPs in the cluster. Formation of Au NP clusters enhanced the calculated maximum field approximately 100 times higher than that of a single Au NP. The numerical results showed that hotspots are created between Au NPs in the SiO₂ shell compartment. Furthermore, the combined result of the LCTEM observation and the numerical result indicated that the hollow particles provide a confined space in which Au NP can form their clusters in order to create hotspots.

The assembled states of Au NPs incorporated into the hollow particles (Au-PMBA@hSiO₂ or mAu-PMBA@hSiO₂) are reversibly controlled via applying an AC electric field in Chapter 6. During the Raman measurement, the external AC field at a frequency of 1 kHz was applied to (m)Au-PMBA@hSiO₂ particle suspensions which

were sealed in a glass capillary with electrodes 1 mm apart. The Raman intensities of PMBA were gradually increased during a 50 V/mm field application for 10 min. The Raman intensities were strongly related to the assembled states of the (m)Au-PMBA@hSiO₂ particles in solution. The assembled states of the (m)Au-PMBA@hSiO₂ after application of the electric field were observed with an optical microscope. Although it was difficult to observe a single hollow particle because of the particle sizes much smaller than visible light wavelengths, the local number densities of the particles in a vicinity of electrodes different from that in a center part of capillary. This experimentally showed that the spatial distribution of the particles was successfully controlled by the electric field. Clear differences of the Raman intensities with and without the electric field were observed more distinctly in the case of mAu-PMBA@hSiO₂ particles compared to those of Au-PMBA@hSiO₂ particles. Raman intensities of PMBA in the presence of the particles were reversibly changed by switching ON and OFF states of the electric field. However, the extinction peaks of the particle suspensions acquired after the field application were almost the same as those without the field application, showing that hotspots for SERS were not created between Au NPs in the shell compartment. The improvement of the sensing properties of the particles indicated that assembling (m)Au-PMBA@hSiO₂ particles with an electric field can be an effective approach to reversibly control the collective properties of plasmonic NPs even if no hotspots are created between the NPs incorporated into different hollow particles.

In Chapter 7, conclusion of the present work is described. In this thesis, we proposed a new system for reversible control over the spatial distribution of Au NPs in a liquid phase. The spatial distribution of Au NPs was successfully controlled using hollow particle structures with the following steps: (i) incorporation of Au NP clusters with the different numbers in hollow SiO₂ particles, and (ii) reversible control over the assembled states of Au NPs incorporated within the hollow particles by switching ON and OFF states of an external AC electric field. The proposed system is applicable to other nano-sized particles which have a low colloidal stability. The system solves the dilemma of agglomeration of particles while they are assembled in a liquid phase, and it possibly leads to enhancement of properties of nanomaterials.

論文審査結果の要旨

金や銀などのプラズモンナノ粒子は、バルク材料とは異なる特性（例えば光学特性、センサー特性）を発現する。ナノ粒子の特性を効率的に引き出すためには、粒子を限られた空間中に集めること、つまり粒子の空間分布を制御することが有用である。一方で、過度な粒子数密度の増大は粒子凝集のリスクを高め、上記特性の低下が予想される。本研究では、中空粒子構造を利用し、金ナノ粒子の空間分布を可逆的に制御可能なシステムの開発を目的とした。

第1章は緒論であり、本研究の背景と目的を述べた。

第2章では、プラズモンナノ粒子の集積状態を制御した既往の研究をまとめた。中でも、外部刺激を用いることで、刺激のON/OFFの切り替えにより粒子空間分布の可逆的制御の実現が期待できることを述べた。

第3章では、外部刺激として交流電場を用いて金ナノ粒子の液中での空間分布制御を試みた。金ナノ粒子懸濁液に電場を印加すると、液中において金ナノ粒子がクラスターを形成することを示した。一方で、一度クラスターを形成した金ナノ粒子は元の分散状態に戻すことは不可能であった。

金ナノ粒子空間分布の可逆的な制御に向け、第4章では金ナノ粒子を内包した中空シリカ粒子の合成を行った。得られた中空粒子の特性は、内包する金ナノ粒子の個数により大きく変化することを示した。

第5章ではまず、中空粒子に内包した金ナノ粒子の液中での運動挙動を観察した。続いて、粒子間に増強される電場強度を数値計算により推定した。本章で得られた各結果は、第4章で得られた実験結果を支持するものであった。

第6章では、合成した金ナノ粒子内包型中空粒子に交流電場を印加することで液中におけるナノ粒子空間分布の可逆的制御を試みた。同中空粒子懸濁液に電場を印加することで局所的な粒子数密度が増加し、得られるプラズモン特性が向上することがわかった。また、電場印加・解除を複数回繰り返してもその特性の切り替えは可能であり、粒子空間分布が可逆的に変化することが示された。

第7章は総括であり、本研究で得られた結果を総括するとともに、今後の展望を述べた。

以上、本論文では中空粒子構造を利用することで凝集しやすいナノ粒子の可逆的な空間分布を制御する手法を示した。本手法は、微粒子材料開発において重要な課題である「ナノ粒子の凝集・分散状態の可逆的制御」を解決するためのアプローチとして、化学工学をはじめ他学問分野の発展に貢献できると考えられる。

よって、本論文は博士(工学)の学位論文として合格と認める。